

# **SYNTHESIS AND SINTERING OF ALUMINA PRECURSOR POWDER PREPARED IN HYDROXYHYDROGEL FORM**

A thesis submitted

by

**Akshay Kumar**

**109CR0675**

In the partial fulfilment of the requirements of degree  
Of  
Bachelor of Technology



DEPARTMENT OF CERAMIC ENGINEERING  
NATIONAL INSTITUTE OF TECHNOLOGY  
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# NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

## CERTIFICATE

This is to certify that the thesis entitled, “**Synthesis and sintering of alumina precursor powder prepared in hydroxyhydrogel form**”, submitted by **Mr. Akshay Kumar (Roll no. 109CR0675)** in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

**Prof. Sunipa Bhattacharyya**

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Date: 11.05.2013

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**Akshay Kumar**

**109CR0675**

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# **ABSTRACT**

Alumina precursor powder is synthesized using aluminium nitrate and ammonia solution in hydroxyhydrogel form. Then characterization of powder is done by XRD, Particle size distribution, BET Analysis, FTIR, DSC and TGA. The powder is calcined at 500°C and pellets are pressed. Sintering of pellets is done at 1650°C. Characterizations of the sintered pellets are carried out by XRD, SEM, Linear shrinkage, Bulk density and apparent porosity measurement.

# CHAPTER-1

## **I**NTRODUCTION



## 1.1INTRODUCTION:

Alumina is a versatile material used as refractory, engineering ceramics material, abrasive and in various other applications where chemical inertness coupled with its high hardness and abrasiveness is of primary importance. It can be prepared from several methods i.e. combustion method, precipitation from various salts and sol-gel method. The chemical synthesis routes play a crucial role in preparing the final product and are better than traditional methods for the production of fine-grained mixed oxide powders, having good physical properties. Fine powders prepared involve shorter diffusion distances in sintering processes and have improved microstructural homogeneity. Chemically synthesized alumina powders are well known for their nanometric-sized particles. [1]

Aluminium hydroxide is common source for preparation of alumina in every method. It exist in various metastable polymorphs in addition to the thermodynamically stable  $\alpha$  alumina form. The structures of all the aluminium hydroxides consist of stacked double layers of oxygen atoms in which the aluminium cations are located in octahedral coordination in the interstices [2]. The packing of oxygen ions inside the layer can be either hexagonal or cubic, whereas the symmetry for each hydroxide is determined by the distribution of hydrogen. The relative distances between hydroxyl groups, both within and

between the layers, have been suggested to control the mechanism of dehydration for the particular hydroxide. This structure of aluminium hydroxide depends on the aluminium hydroxide precursors which in turn may be influenced by the aluminium salts used as the starting reagents as well as on the procedure by which the precursors have been prepared.[3]

# CHAPTER. 2

LITERATURE

REVIEW

## 2.1 REVIEW

Rodica ROGOJAN et al. [4] has Prepared alumina powder by sol gel method can be done using organic precursors and inorganic precursors. Two precursors used in synthesis of alumina by sol-gel method were of different chemical nature: inorganic- aluminum chloride and organic aluminum triisopropylate. Both precursors are subjected to 20% ammonia and a gel formation is there. The resulting gel is applied to heat treatment above 1000° C then characterization of powder by X-ray diffraction, Differential thermal analysis, scanning electron microscopy, transmission electron microscopy etc... is done. Applying a heat treatment at temperatures higher than 1000°C only single phase  $\alpha$ - alumina is obtained. By sol-gel method using organic or inorganic precursors after a heat treatment in both case nano alumina powder is obtained. Alumina powder in nano size has better properties than large particle size powder.

D.Thomazini et al. [1] have prepared alumina nano powder by pechini method and emulsification method and studied the sintering of both type of powder by conventional sintering and microwave sintering method. The samples obtained by microwave sintering presented a finer microstructure than those produced by conventional sintering. This may have resulted from the high heating rate, which favours the sintering process by boundary diffusion. The commercial

alumina reaches densification (99.2% of TD) in less time by the microwave sintering process than in the conventional one due to the direct transfer of microwave energy to the samples, which accelerated the densification process. The ceramics produced with chemically synthesized alumina powders did not densify but density values reached results slightly close the ones obtained in the conventional furnace, even being heated for less time. This is due to their low values of green density, which hindered the densification process.

Thermal behaviour of alumina powder prepared from different salts also shows different formation temperature of  $\alpha$ -alumina and  $\gamma$ - alumina [5]. Aluminium hydroxide has been precipitated from various aluminium salts and differences in their thermal behaviour are investigated. Heating the samples to 1000°C without holding at temperature sharpens the gamma-Alumina reflections. The presence of delta-Alumina in these samples cannot be ruled out since they could be contained within the broad diffraction profile, but no evidence of  $\eta$ -Alumina is present in any of the samples at this temperature. The high-temperature thermal behaviour of alumina precursors synthesized under identical conditions changes when different aluminium salts are used as the starting reagents. In particular, aluminium hydroxide prepared by precipitation from aluminium sulphate transforms more readily to corundum at 1100–1200°C than hydroxides prepared from the nitrate or the chloride,

even though the thermal reactions of all three compounds below 1000°C are similar. The difference in high-temperature behaviour is probably related to the presence of basic sulphate species carried over in the precipitated pseudoboehmite. These species are thermally stable at temperatures > 600°C, but eventually decompose with the formation of a pore structure which facilitates the nucleation of  $\alpha$ -Alumina.

There are other methods to synthesis of alumina powder which shows that powder prepared from different route has different particle size. Stability and sintering properties are affected by particle size. Two other methods are studied which produced different size of alumina properties and show different sintering behaviour [6]. Synthesis of alumina powder is done by HP (Homogenous precipitation) and POI (Polymerized organic -inorganic). Both methods is characterized by SEM, X-RAY diffraction with temperature change, crystal evaluation, powder microstructure and particle size, type of sintering and shrinkage during sintering. At 850 °C only one phase ( $\gamma$ - alumina) is present but in POI method ( $\gamma$  and  $\alpha$ -alumina) present. Comparing particle sizes obtained by both methods H provide better than P in terms of stabilizability to reach the best densification after sintering, powders obtained by POI method behave more suitable. HP produces nano powder and POI produces micro powder.

Hydroxyhydrogel (HHG) and normal gel (NHG) both can be prepared from same precursors by varying the mode of addition [7]. Aluminium hydroxide prepared in both cases is characterized to get over all chemical changes and reactivity formed by two different routes. HHG contains more amount of water than NHG. Rate of dehydration of water is higher for HHG than NHG; however at higher temperature they converge. It appeared from IR analysis that Al was predominantly in the octahedral coordination in HHG sample, whereas in NHG, both octahedral and tetrahedral coordinated Al was present. This was particularly observed when specimens were heat treated at 700°C temperature. The second major difference is the absence of gibbsite peak in the HHG samples. Presence of gibbsite phase indicates the presence of directed bonds between OH groups of adjacent layers rendering hydrogen bonds in the plane of the OH groups longer than those between the layers. These results in shortening of the shared ages of  $\text{Al}(\text{OH})_6$ , i.e. hexacoordinated Al were found in both the sample but for NHG sample tetra-coordinated Al are also noticed.

## **2.2 Plan of work**

a) Alumina precursor powder synthesis using aluminium nitrate and ammonia solution in hydroxyhydrogel form.

b) Characterization of powder:

i) TGA /DSC

ii) Particle size distribution

iii) Surface area measurement

iv) X-Ray diffraction

v) FTIR

c) Fabrication of pellets

d) Sintering of pellets

e) Characterization of sintered pellets

i) Apparent porosity

ii) Bulk density

iii) Linear shrinkage

iv) XRD

v) SEM



# **CHAPTER. 3**

**E**XPERIMENTAL

**P**ROCEDURE

## **EXPERIMENTAL PROCEDURE:**

### **Chemicals used:**

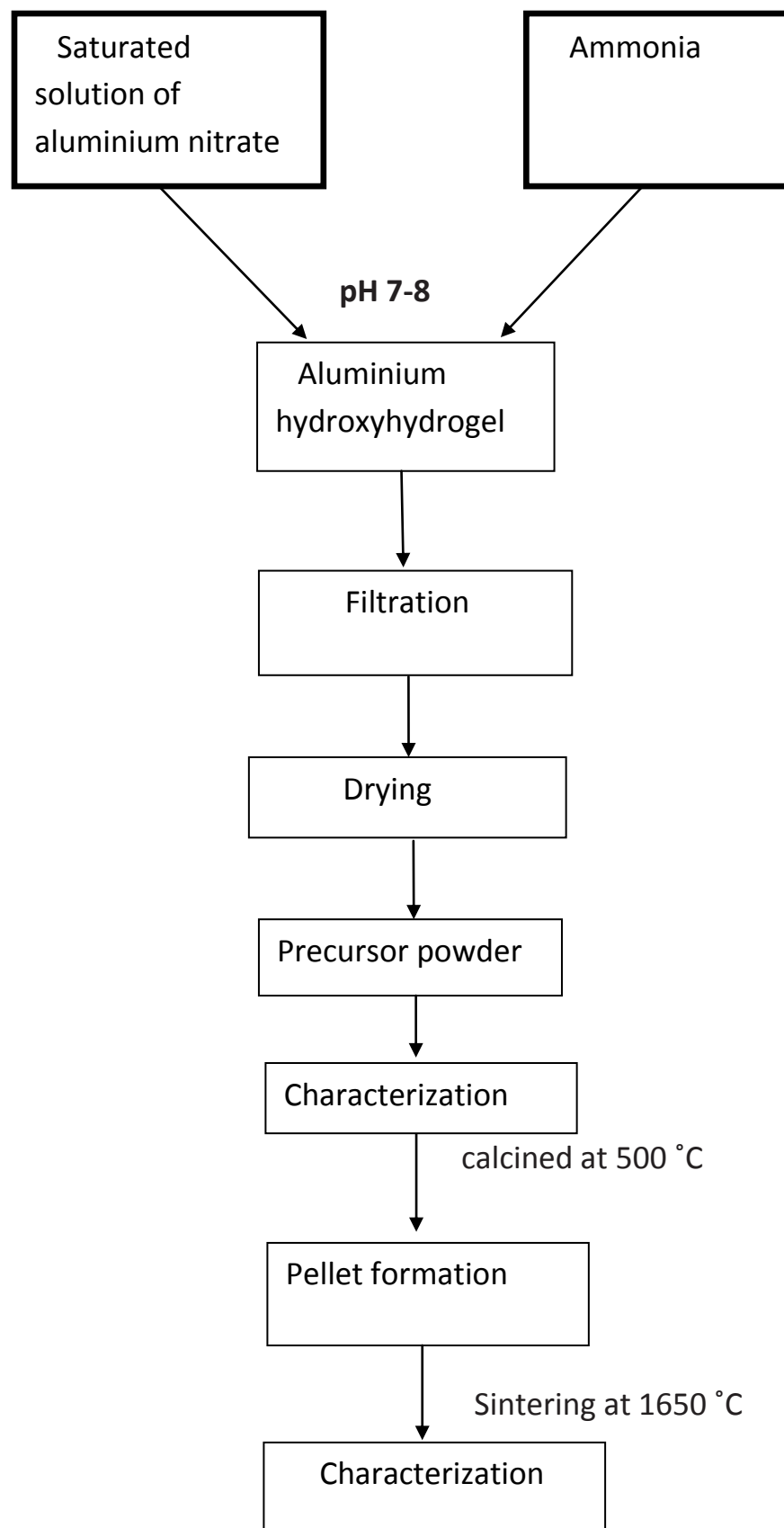
Aluminium nitrate, ammonia and distilled water

### **Apparatus required:**

- 1) Two 100 ml beakers
- 2) One 50 ml beaker
- 3) Glass rod
- 4) Magnetic stirrer
- 5) pH paper
- 6) Filter paper
- 7) Funnel
- 8) Petridis
- 9) Heater

## Procedure:

### Flowchart:



First we take around 100 ml of distilled water and after that aluminium nitrate salt is added to form saturated solution of aluminium nitrate. Small amount of aluminium nitrate is added to distilled water with continuous stirring till saturated solution is formed and left for one day. 8ml of 20 % ammonia solution is required for 12 ml saturated solution of aluminium nitrate to complete reaction or maintain the pH 7. In a beaker 100ml of saturated solution of aluminium nitrate is taken and 66 ml of ammonia is added. Then white colour precipitate of aluminium hydroxide is formed. Then washing with hot distilled water is done and precipitate is filtered using Buckner funnel. The precipitate is taken out in a Petridis and dried at 100°C for 5 hours to removal of physical water. After 5 hours the dried HHG is taken out and powder is formed. Powder of alumina is formed using aged mortar. The powder is kept in desiccator because it can absorb physical water. The powder is calcined at 500 °C, 600 °C, 700 °C, 800 °C, 1000 °C and 1100 °C for 1 hour each. Then characterization of powder is done.

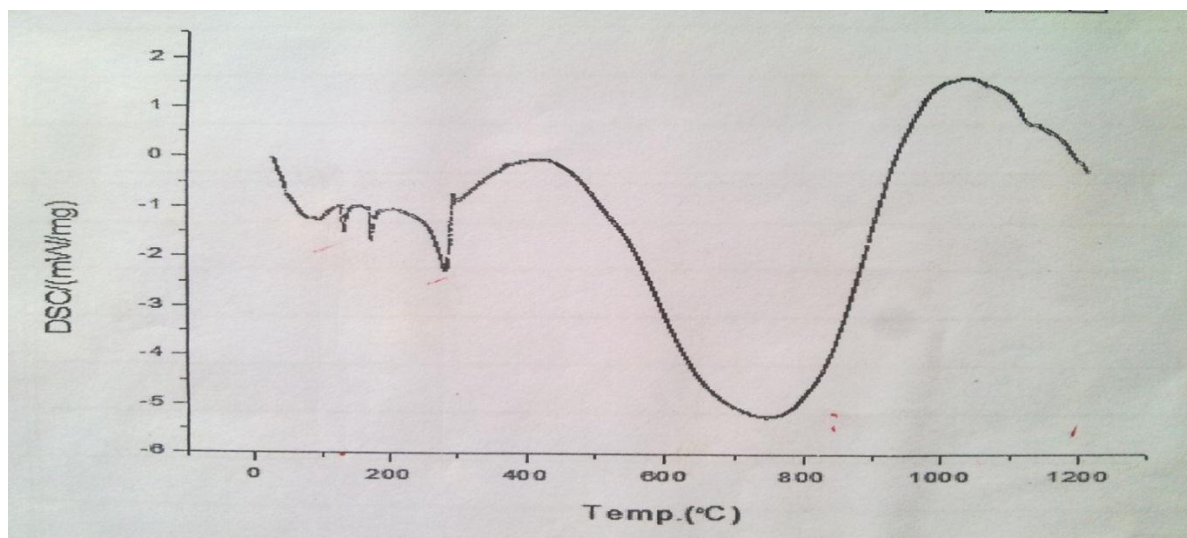
The powder is calcined at 500°C and pellets are formed using hydraulic pressing machine. The pressure is kept 4 ton for 90 seconds. And dimensions are measured. The pellets are sintered at 1650°C and characterized.

# **CHAPTER. 4**

**R**ESULTS AND

**D**ISCUSSION

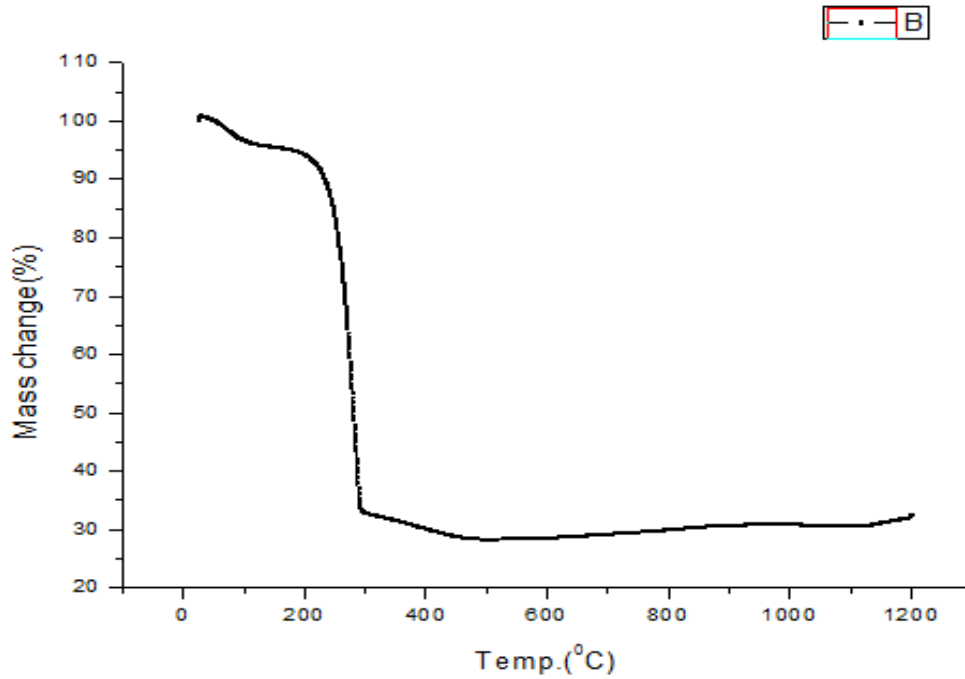
### Discussion:



**Fig.1 – DSC analysis of alumina powder**

Graph indicates that endothermic peak around 120°C is due to elimination of absorbed water. And an endothermic peak at 180°C and 280°C is due to decomposition of chemically bonded water. There is one exothermic peak at 300 °C due to transition from aluminium hydrate to ordered alumina. The endothermic effect at 780 °C may be attributed to the transformation of polymer phase enantiotrope of  $\gamma$ -alumina to  $\alpha$ -alumina.

1



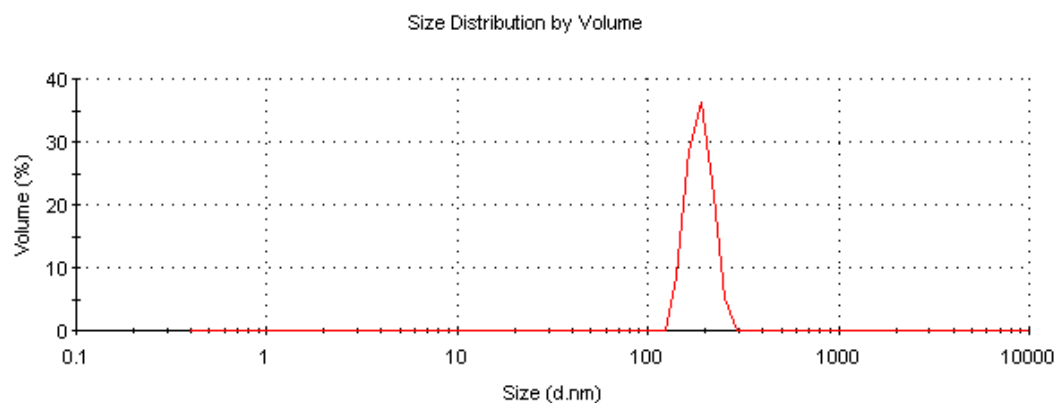
**Fig.2 TG analysis of alumina powder**

The weight loss in sample occurs in three stages.

- 1) Weight loss of around 5% from room temperature to 100 °C due to decomposition of surface water.
- 2) Weight loss of around 62% from 100 °C to 280 °C due to decomposition of hydroxyl group.
- 3) Weight loss of around 6% from 280 °C to 450 °C due to decomposition of chemically bonded hydroxyl.

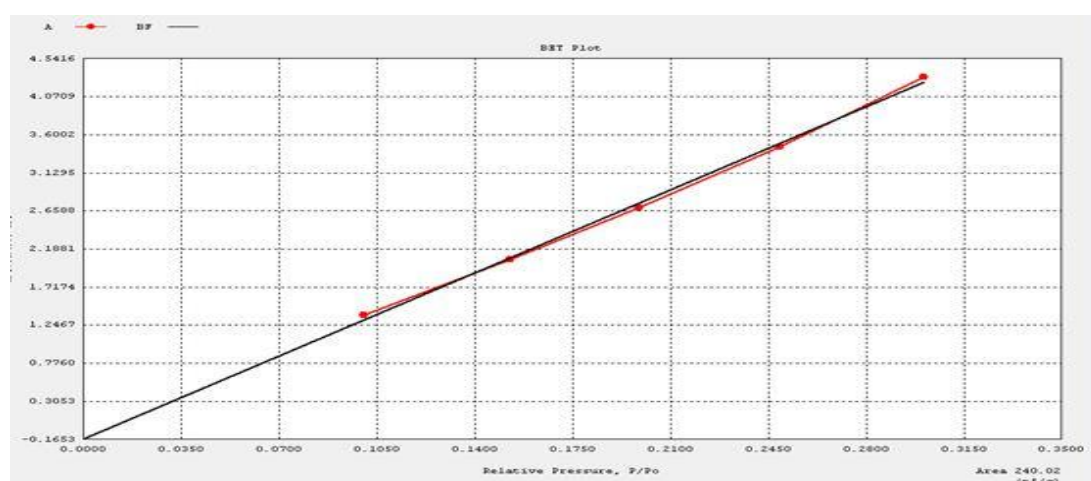
## Particle size distribution:

It shows that maximum volume 35 % of particles have diameter around 180 nm and particle's diameter range is 110 to 190 nm.



**Fig. 3- Particle size distribution**

**BET Analysis:** This technique is used to measurement of specific area of material. The surface area of alumina powder is  $2.4 \text{ m}^2/\text{gm}$ .



**Fig.4- Surface area measurement**



**Powder calcination:** The powder is calcined at 500 °C, 600 °C, 700 °C, 800 °C, 1000 °C and 1100 °C for 1 hour each. And XRD of the calcined powder is done. The X-ray diffractograms of the samples heated to 800°C without holding at temperature indicate that at this temperature powder formed is poorly crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This result is consistent with the DTA observation that the endothermic peak due to the crystallization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

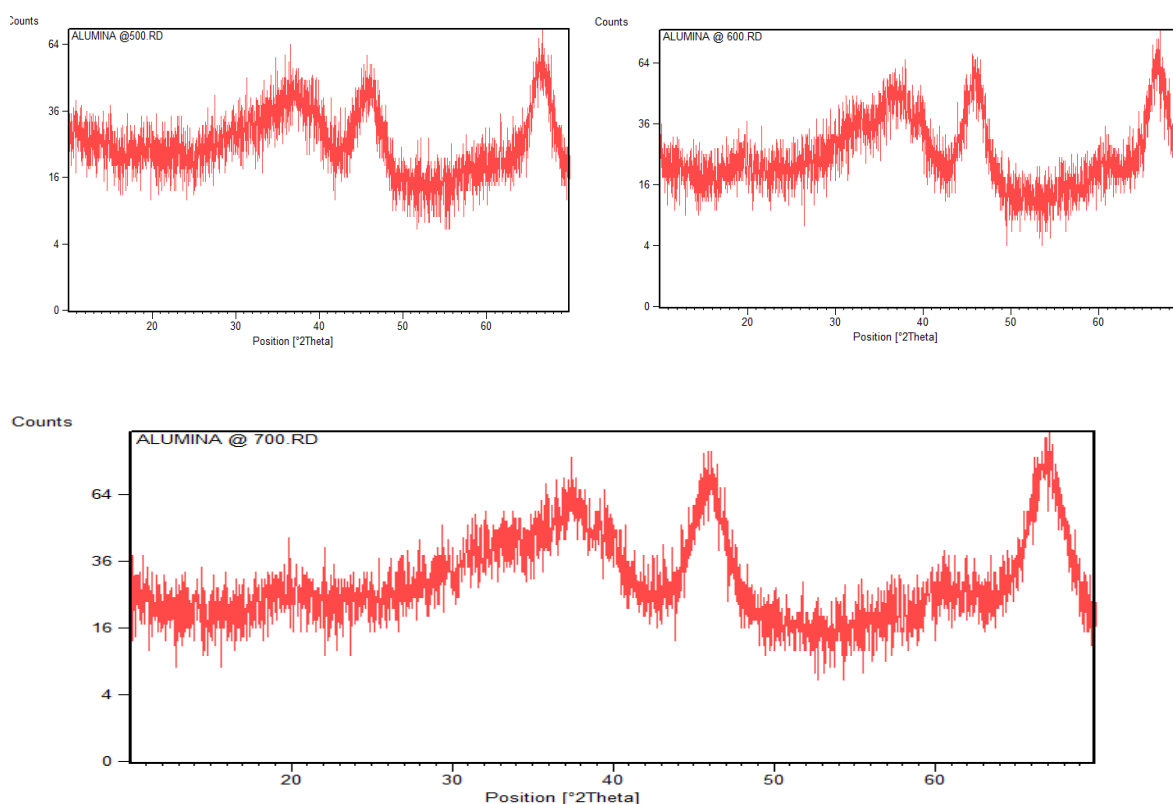


Fig.5 XRD of alumina powder calcined at 500 °C

Fig.6 XRD of alumina powder calcined at 600 °C

Fig.7 XRD of alumina powder calcined at 700 °C

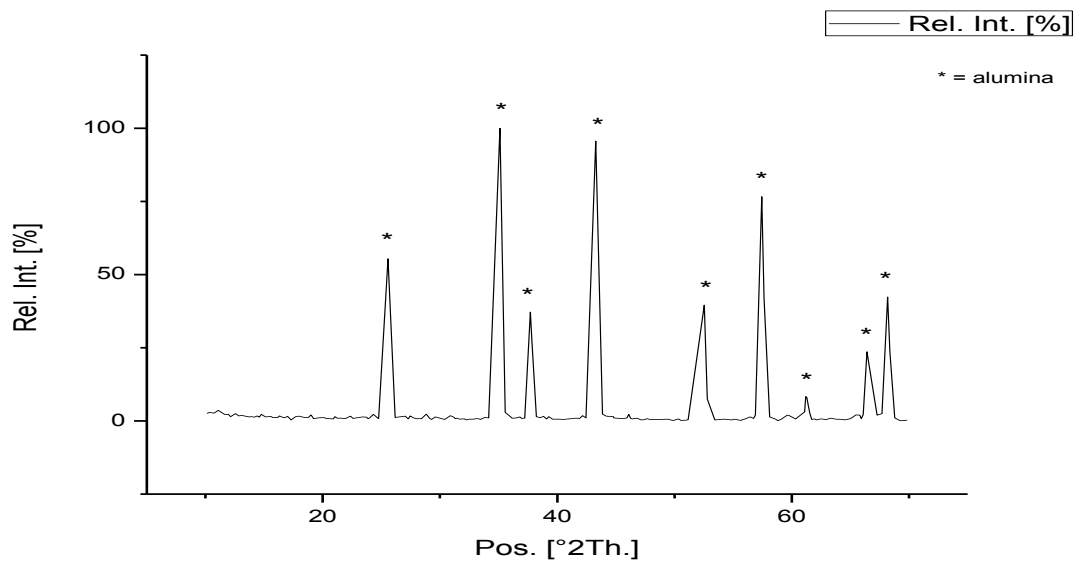


Fig.8- XRD of alumina powder calcined at 1100°C

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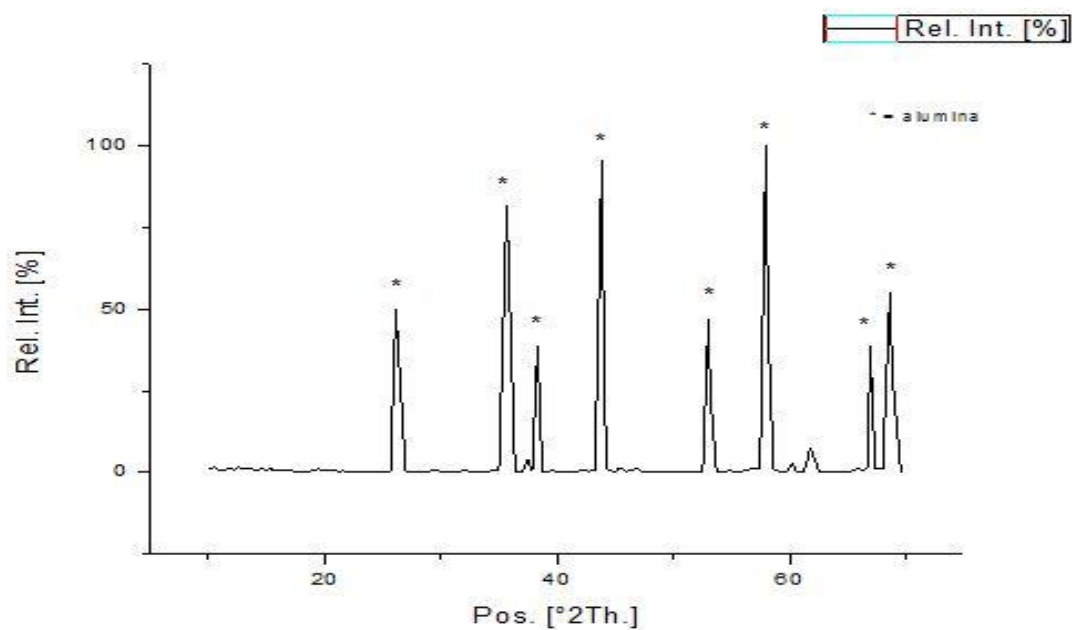
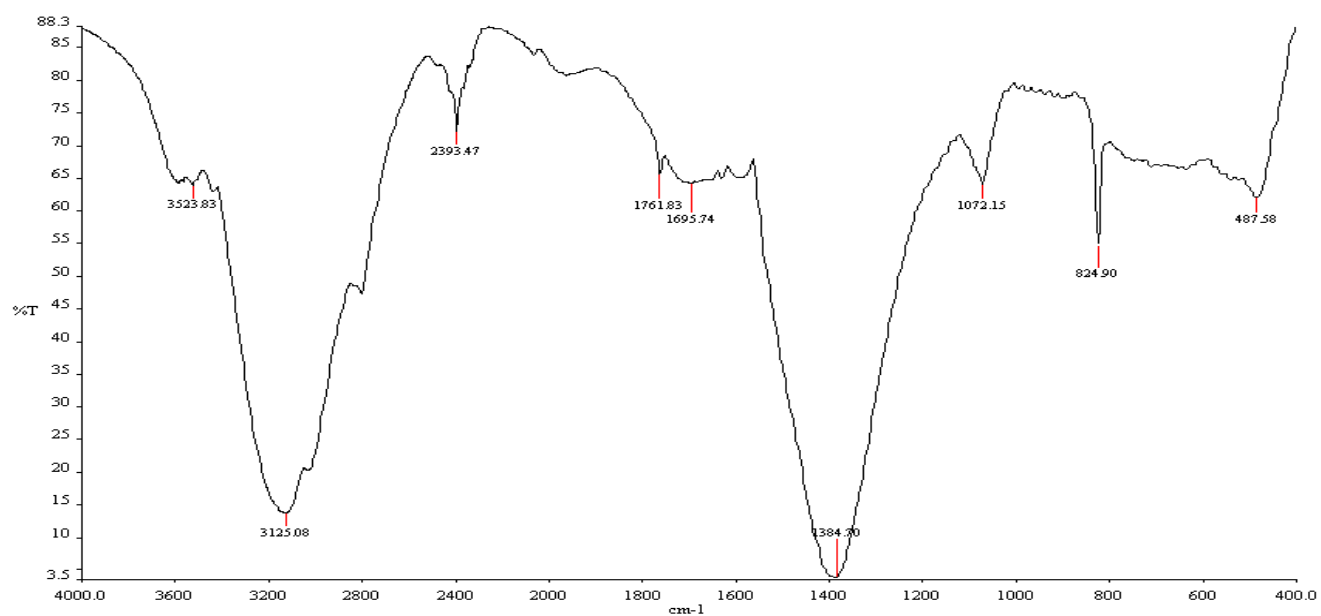


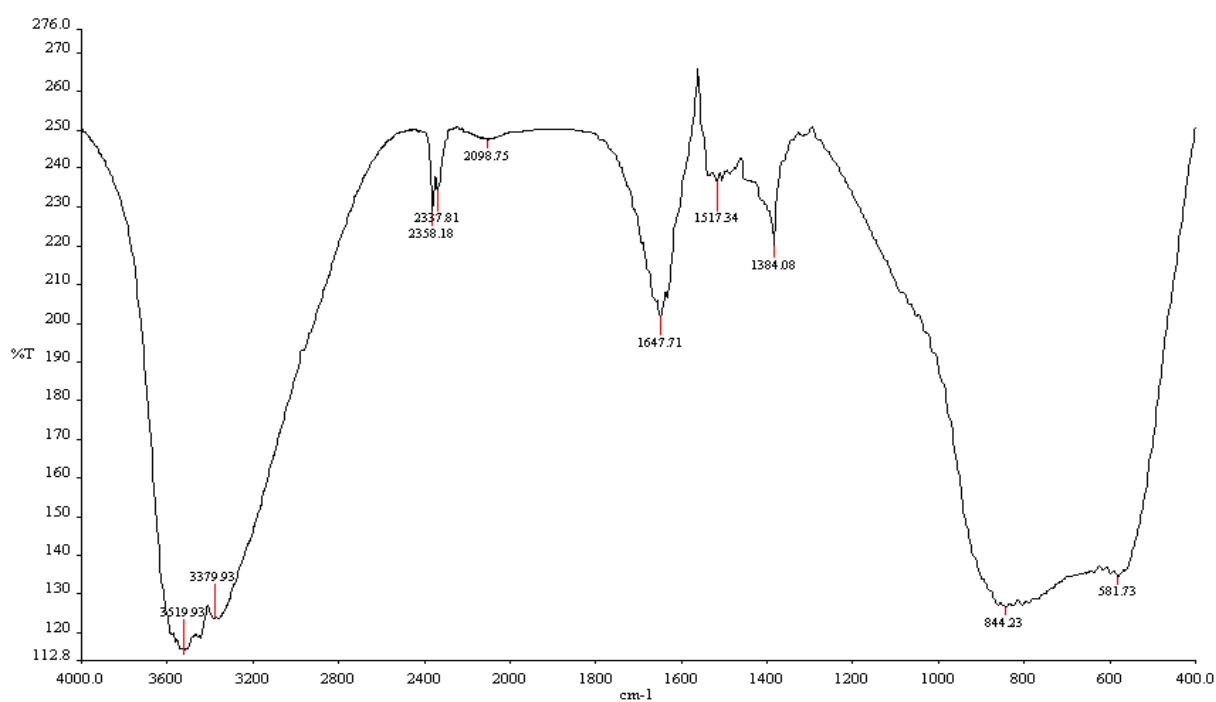
Fig.9 - XRD of sintered pellet at 1650°C

XRD of alumina powder calcined at 1100 °C shows all peaks correspond to  $\alpha$ -alumina. Up to 800°C there are spurious peaks corresponding to  $\gamma$ -alumina

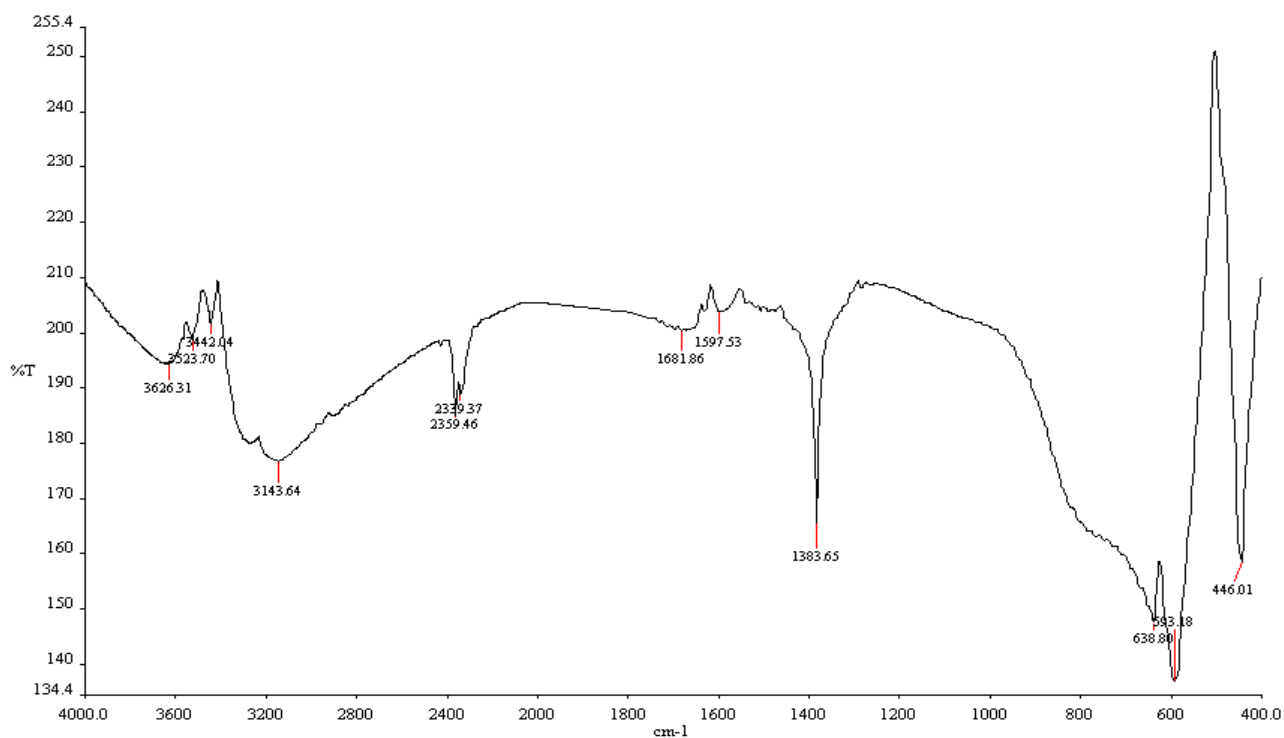
phase that is supported by result coming from DSC analysis i.e. the conversion of  $\gamma$ -alumina to  $\alpha$ -alumina occurs above 1000°C.



**Fig.10 – FTIR analysis of alumina powder (uncalcined)**



**Fig.11- FTIR analysis of powder calcined at 500°C**



**Fig.12- FTIR analysis of alumina powder calcined at 1100°C**

The absorption band in the range of 3600-3100 cm<sup>-1</sup> represents OH stretching vibration connected to Al<sup>3+</sup>. Absorption band around 1650 cm<sup>-1</sup> and 1384 cm<sup>-1</sup> indicate bending mode of water and nitrate, presence of both hydroxide stretching mode and bending mode of water molecules was in agreement with the presence of both water and OH group in the powder precursor. The IR spectra of 1100°C calcined powder contain both O-H stretching & bending mode that imply some hydroxyl group still present and their bond strength are high. Absorption band at 1072 cm<sup>-1</sup> represents Al(OH)<sub>3</sub> characteristic band. Al-

O stretching mode for tetrahedral coordinated  $\text{Al}^{+3}$  is represented by the absorption band around  $800\text{ cm}^{-1}$  whereas absorption band in the range of  $450\text{-}600\text{ cm}^{-1}$  represents Al-O stretching mode of octahedral coordinated  $\text{Al}^{+3}$ . Both for uncalcined and calcined at  $500^\circ\text{C}$  powder the presence of  $\text{AlO}_4^-$  tetrahedral and  $\text{AlO}_6$  octahedral is predominant whereas in  $1100^\circ\text{C}$  calcined powder Al-O bonds for transition alumina develops into two or three small bands at around  $639$ ,  $593$  and  $446\text{ cm}^{-1}$ . The corundum structure is build up only an octahedral  $\text{AlO}_6$  and the most characteristic IR feature is the occurrence of two strong bonds near  $650\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$  together with some others at  $450\text{ cm}^{-1}$ . So  $1100^\circ\text{C}$  calcined powder is purely corundum ( $\alpha$ -alumina) that is also supported by XRD & DSC study.

**PELLETS FORMATION:** Pellets are formed using  $500^\circ\text{C}$  calcined powder and dimensions are measured.

**Table.1- Dimensions of green bodies (pellets):**

Pellet No.	Diameter(mm)	Thickness(mm)	Weight(gm.)
1	12.64	5.35	0.934
2	12.65	5.29	0.918
3	12.64	5.40	0.940
4	12.64	5.50	0.964
5	12.65	5.40	0.947
6	12.64	5.30	0.923

The average green density is 1.389 gm./ cc. Sintering of pellets is done at 1650° C for 2 hours and again dimensions are measured.

**Table.2- Dimensions of sintered pellets:**

Pellet No.	Diameter(mm)	Thickness(mm)	Weight(gm.)	Linear shrinkage (%)
1	9.22	4.04	0.816	27
2	9.22	3.96	0.8038	27.1
3	9.20	4.05	0.8174	26.97
4	9.24	4.13	0.8412	27
5	9.22	4.07	0.8201	27.1
6	9.22	3.98	0.8106	26.99

The average linear shrinkage is 27.04 %.

**Table.3- calculation of bulk density and apparent porosity:**

$$\text{Apparent porosity} = \frac{W-D}{W-S} \times 100$$

$$\text{Bulk density} = \frac{D}{W-S}$$

Where D- Dry weight

S- Suspension weight

W- Soaked weight

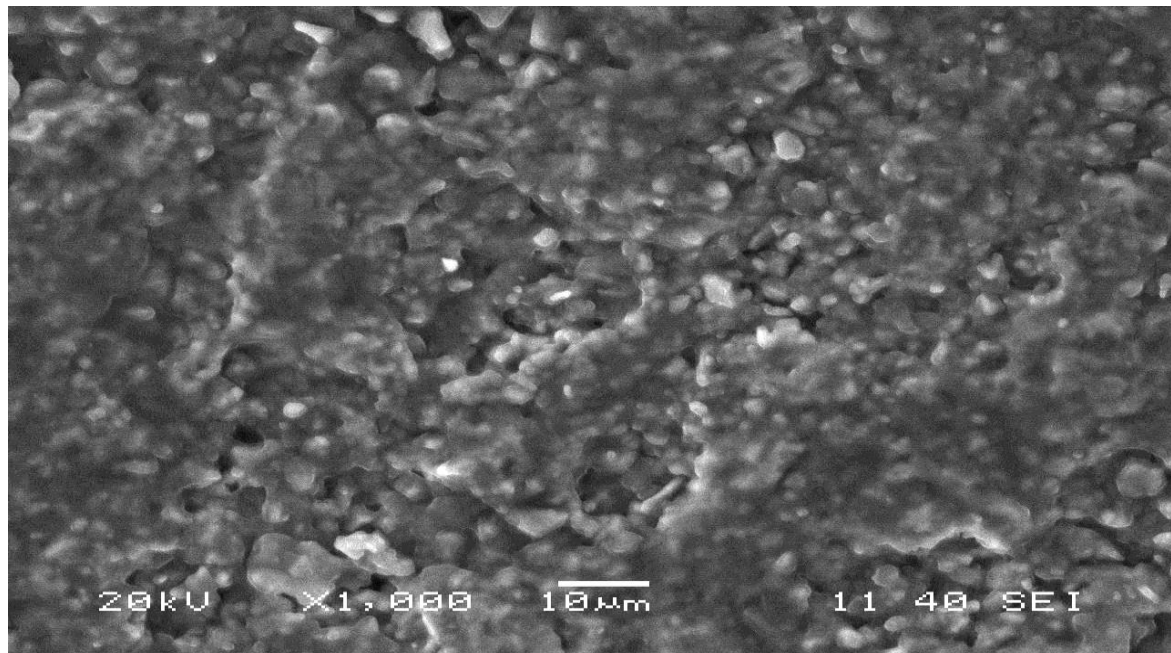
Pellet No.	Dry wt.(gm.)	Suspension wt.(gm.)	Soaked wt.(gm.)	Apparent porosity(%)	Bulk density
1	0.820	0.6027	0.8659	17.43	3.115
2	0.806	0.6004	0.8549	19.21	3.16
3	0.819	0.6023	0.8650	17.51	3.117
<b>average</b>				<b>18.05</b>	<b>3.131</b>

The lower green density of the samples is about 34% of true density illustrates the difficulty in final densification of material. Low compaction can be attributed to fact that since the precursor powder is very reactive so they have a great tendency to agglomeration. These agglomerates after calcination converted to hard agglomerate which cause compaction problem and hamper

densification. So at 1600°C maximum density is achieved only around 80 % of theoretical density.

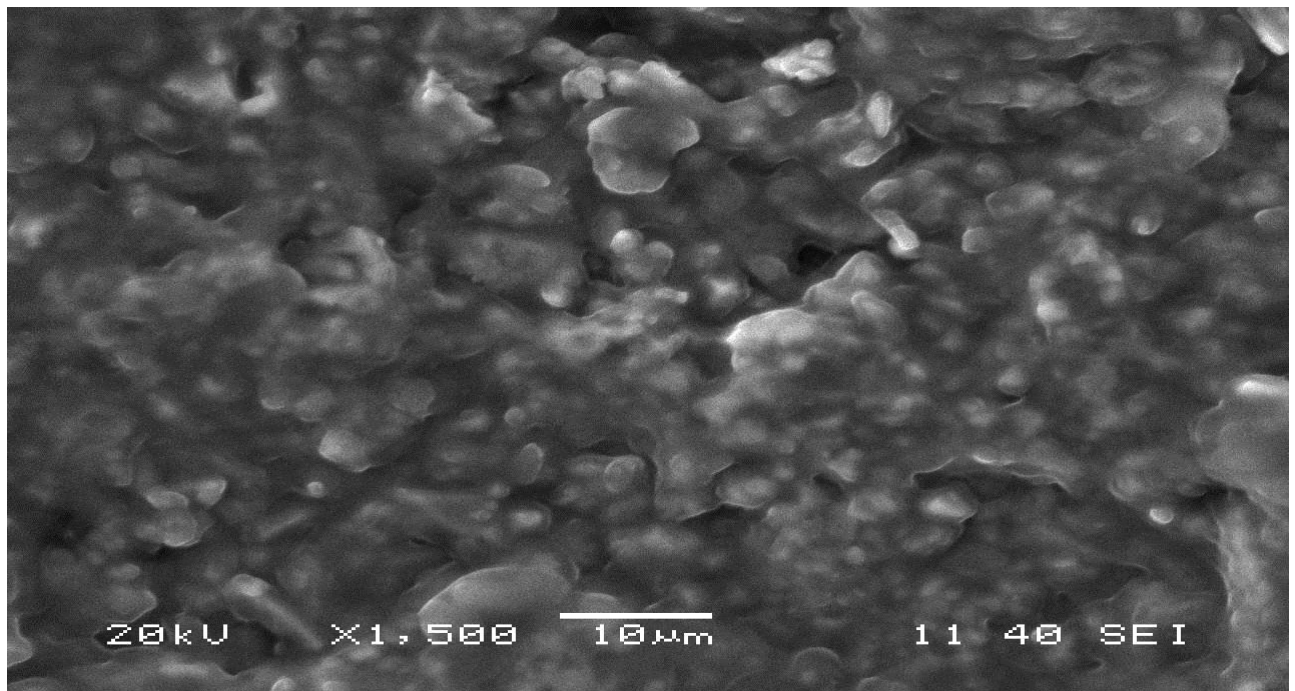
### **SEM analysis:**

SEM analysis of sintered pellet (1650°C) is done to see the microstructure after sintering. The sample are mounted on the sample holder and put inside the SEM.



**Fig.13(a)- SEM image of sintered pellet (x1000)**





**Fig.13 (b) - SEM image of sintered pellet (x1500)**

From micrograph it was found that pores are present, particle neck formation started but completed due to presence of hard agglomeration, after calcination compaction problem arises and densification is hampered.

# **CHAPTER 5**

## **C**ONCLUSIONS

**From these experiments it is concluded that:**

By this hydroxyhydrogel method we are able to prepare alumina precursor powder which can be easily converted to  $\alpha$ -alumina at comparatively lower temperature (1100°C) or may be less than 1100°C. But the presence of agglomeration after calcination prevents or hindered densification at higher temperature.

# **CHAPTER 6**

## **R**EFERENCES

- [1] D. Thomazini, M. V. Gelfuso, Alumina ceramics obtained by chemical synthesis using conventional and microwave sintering *Cerâmica* 57 (2011) 45-49, brazil, 1321
- [2] K. Wefers, C. Misra, Oxides and Hydroxides of Aluminium, Alcoa Technical Paper No. 19, Alcoa Laboratories, Pittsburgh, PA, 1987.
- [3] J. Temuujin, Ts. Jadamba, K.J.D. Mackenzie, P. Angerer, Thermal formation of corundum from aluminium hydroxides prepared from various aluminium salts, *Bull. Mater. Sci.* 23 (4) (2000) 301–304.
- [4] Rodica ROGOJAN, Ecaterina ANDRONESCU Synthesis and Characterization of alumina nano powder obtained by sol-gel method. *U.P.B. Sci. Bull., Series B*, Vol. 73, Iss. 2, 2011
- [5] R. ROMÁN, T. HERNÁNDEZ, and M. GONZÁLEZ, Nano or micro grained alumina powder? A choose before sintering, *Bol. Soc. Esp. Ceram. V.*, 47, 6, 311-318 (2008)
- [7] T. Meher, A.K. Basu, S. Ghatak, Physicochemical characteristics of alumina gel in hydroxyhydrogel and normal form, *Ceramics International* 31 (2005) 831–838